

A COMPLETE COLLECTION OF THERMODYNAMIC
FORMULAS.

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IN this paper is presented a complete and systematic collection of thermodynamic formulas involving the first and second derivatives of the ordinary thermodynamic quantities. It has been possible to compress such a collection into a reasonable compass by a short-hand method of expression. The fundamental quantities whose various relations are treated in the tables are ten in number; namely p , v , τ , E , s , Q , W , H , Z , and Ψ . It will be remarked that the specific heats are not included in the fundamental ten quantities. This is because the specific heats are properly first derivatives, $C_p = \left(\frac{\partial Q}{\partial \tau}\right)_p$, and $C_v = \left(\frac{\partial Q}{\partial \tau}\right)_v$. These ten quantities, with their first and second derivatives, are connected by various relations. The relations between the quantities themselves are simple, and mostly of the nature of definitions. But the relations between the first and second derivatives are more complicated, and it is these which are of special interest.

We consider first the first derivatives. The conditions imposed by the first and second laws of thermodynamics and the particular properties of the substance under consideration are such that every derivative of the type $\left(\frac{\partial W}{\partial \tau}\right)_q$ has a definite meaning. This derivative means that the particular body in question is allowed to change so that Q remains constant, that is, no heat is absorbed, and the ratio of the change of W to the change of τ found during this change.¹ Every first derivative involves, therefore, three different variables, and it is at once seen that the total number of such derivatives is 720 ($= 10 \times 9 \times 8$). These 720 derivatives are connected by various relations, and in general there is an equation connecting any four of them and certain of the fundamental ten quantities. There are, therefore,

$$\frac{720 \times 719 \times 718 \times 717}{1 \times 2 \times 3 \times 4} = 11,104,365,420$$

such relations between the first derivatives.

¹ It should be noted that although the derivatives always have a meaning in the sense indicated, the functions which are being differentiated need not be expressible as functions of the position coordinates. W and Q are such functions; it is impossible to assign any meaning to them as functions of p and τ for example, but still the variations of W and Q in definite directions are entirely determined.

A complete collection of first derivatives would involve the tabulation, therefore, of these 11,104,365,420 relations. This of course is absolutely out of the question; the best we can do is to tabulate some of the derivatives in such a form that any of the derivatives may be obtained by slight and obvious effort. We evidently shall attain this object if every one of the 720 first derivatives is tabulated in terms of the same three fundamental derivatives. To obtain any desired one of the numerous relations between any four derivatives, therefore, we merely have to eliminate the three fundamental derivatives between the four equations for the four derivatives.

The three fundamental derivatives may be chosen in a great variety of ways. The three chosen here are the three which are perhaps given most directly by experiment; the isothermal compressibility $\left(\frac{\partial v}{\partial p}\right)_\tau$, the isopiestic dilatation $\left(\frac{\partial v}{\partial \tau}\right)_p$, and the specific heat at constant pressure C_p . The first two of these may be obtained from the characteristic equation of the substance, that is, the relation connecting p , τ , and v . To determine C_p , calorimetric measurements must be made in addition to the measurements for the characteristic equation. It may be proved that C_p is completely determined, if in addition to our knowledge of the characteristic equation, C_p is known along some line not at constant temperature. Such information, for instance, would be given by a determination of C_p as a function of temperature at atmospheric pressure.

It should be remarked that the method used here of tabulating the 720 derivatives in terms of the same fundamental three will largely do away with the necessity for determining the other relations by an elimination, as suggested above. For if in any special problem every quantity of interest is kept in terms of the same fundamental three, which are independent, one may be sure that at the end of the discussion there are no essential relations not brought to light.

It is now possible to still further reduce the number of expressions needed. To do this, the 720 derivatives may be divided into groups, the variable kept constant during differentiation being kept constant in each group. There are, therefore, ten of these groups, 72 to a group. Let us suppose, for example, that the group is that in which p is the constant element. Any one of the 72 derivatives of this group is of the type $\left(\frac{\partial x}{\partial y}\right)_p$, where x and y are any two of the nine remaining of the ten fundamental quantities. Now let us write, merely as a matter of notation, $\left(\frac{\partial x}{\partial y}\right)_p \equiv \frac{(\partial x)_p}{(\partial y)_p}$. The abridgement in the number of required formulas

is suggested by noticing that we may tabulate $(\partial x)_p$ and $(\partial y)_p$ separately as appropriate functions of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p , and always get the right value for the derivative by replacing $(\partial x)_p$ and $(\partial y)_p$ by these functions and taking the ratio. But there are only nine such expressions in any group, so that we have reduced the number of expressions needed from 720 to 90.

To prove the possibility of splitting up a derivative in the way above is simple. We have the mathematical identity $\left(\frac{\partial x}{\partial y}\right)_p \equiv \left(\frac{\partial x}{\partial \alpha}\right)_p / \left(\frac{\partial y}{\partial \alpha}\right)_p$ where α is any variable, not even necessarily one of the fundamental ten, which remains the same throughout the group of 72. If therefore, we replace $(\partial x)_p$ by $\left(\frac{\partial x}{\partial \alpha}\right)_p$, and similarly $(\partial y)_p$ by $\left(\frac{\partial y}{\partial \alpha}\right)_p$, we shall always obtain the right answer when we take the ratio of any two such functions to find the derivative. It is especially to be noticed that $(\partial x)_p$ is not equal to $\left(\frac{\partial x}{\partial \alpha}\right)_p$; in fact, $(\partial x)_p$ in general does not have the same dimensions as $\left(\frac{\partial x}{\partial \alpha}\right)_p$. The finite functions replacing the differentials have meaning only when the *ratio* of two is taken.

Finally it is possible to further reduce the number of expressions from 90 to 45. We notice that α , of the paragraph above, is not subject to any essential restriction—any function will do. There are ten of these α 's. We may now impose a restriction, making $(\partial x)_p = -(\partial p)_x$, thus reducing to one half the number of fundamental functions. The proof of this will not be given here, but it may be readily seen on writing out the derivatives of the various groups that if an α is chosen so that the relation is satisfied for one derivative of a group, then it will be satisfied by all the others also. The α 's so restricted are not completely determined by any means, but the derivatives, which only we are interested in, are now nearly determined. There is still a certain amount of arbitrariness left, in that the entire collection of functions replacing the partial differentials may be modified by the addition of any factor, but otherwise the functions are determined. This arbitrary factor will be so chosen as to make the functions as simple as possible.

In the actual derivation of the formulas, the α 's play no part; they are simply the mathematical scaffolding used in proving the possibility of replacing the differentials by finite functions, and may now be completely discarded. The method actually used in deriving the formulas was to find a sufficient number of derivatives by well established methods,

and then to split them up, by inspection, into the functions replacing numerator and denominator.

We turn now to a consideration of the second derivatives. The number of combinations of second derivatives is so great that it cannot be reduced to a reasonable number, as could the number of combinations of first derivatives. All that we can do here is to tabulate a sufficient number of the fundamental second derivatives so that any relation existing between them may be found readily by such purely formal mathematical operations of differentiation or elimination as are in the mathematical equipment of every one.

The problem in the case of the second derivatives is analogous to that for the first derivatives; namely to express everything in terms of the same fundamental second derivatives. It may be shown that in general there are four such second derivatives, and for use here we choose the four most directly given by experiment, $\left(\frac{\partial^2 v}{\partial p^2}\right)_\tau$, $\frac{\partial^2 v}{\partial p \partial \tau}$, $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$, and $\left(\frac{\partial C_p}{\partial \tau}\right)_p$.

Suppose now that we wish to find any second derivative. The general second derivative is of the type $\left[\frac{\partial}{\partial x_1} \left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5}$. This is mathematically equivalent to $\left[\frac{\partial}{\partial p} \left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5} \cdot \left(\frac{\partial p}{\partial x_1}\right)_{x_5}$. But $\left(\frac{\partial p}{\partial x_1}\right)_{x_5}$ is a function of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p , which is already known from the tables for the first derivatives. Furthermore, $\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}$ is also a known function of the same three fundamental derivatives, so that $\left[\frac{\partial}{\partial p} \left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5}$ may be found by a purely formal differentiation, if we know $\left(\frac{\partial}{\partial p}\right)_{x_5}$ of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p . There are 27 such second derivatives. The only exception to this scheme of treatment is when $p \equiv x_5$, in which case we have an indeterminate form to evaluate. This may be avoided by taking τ instead of p as our auxiliary variable of differentiation. The differentiation in this case is so simple that it may be performed by inspection.

From these 27 second derivatives we may obtain by a simple formal differentiation any of the 64,800 second derivatives. Each of these second derivatives involves, besides certain of the ten original quantities

and the three fundamental first derivatives, only four independent second derivatives. Hence by eliminating these four second derivatives between the equations for any five second derivatives, we may obtain the relation between any combination of five second derivatives. There are approximately 9.5×10^{21} such relations.

The tables follow. These are given in three parts. First are the fundamental ten quantities with their equations of definition; second the tables in abbreviated form for the first derivatives; and lastly the 27 second derivatives necessary in obtaining any of the 64,800 second derivatives.

TABLE I.

The Fundamental Ten Quantities.

In this table are given the notation and the definition of the fundamental ten thermodynamic quantities. It is to be understood that all the quantities refer to unit amount of the substance. This unit is usually chosen either as 1 gm., or as the quantity that at 0° C. and atmospheric pressure occupies a volume of 1 c.c.

p = pressure per unit area.

τ = temperature on the absolute thermodynamic scale.

v = volume of the unit quantity of the substance.

s = entropy, defined by the integral, $\int dQ/\tau$.

Q = heat absorbed, measured in the mechanical units appropriate to p and v . A physical meaning can be given only to dQ , the heat absorbed during a given change.

W = work done by the substance, in the appropriate mechanical units. Here again, only dW has a physical meaning.

E = the internal energy of the substance in mechanical units. E may be changed by an additive constant without changing its physical meaning. E is one of the thermodynamic potential functions.

$H = E + pv$, the "total heat," also one of the potential functions.

$Z = E + pv - \tau s$, the Gibbs thermodynamic potential.

$\Psi = E - \tau s$, also a thermodynamic potential, the "free energy" of Helmholtz.

TABLE II.

The First Derivatives.

This contains the abbreviated notation by which any of the 720 first derivatives may be found in terms of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p . For instance, if $\left(\frac{\partial E}{\partial \tau}\right)_p$ is desired, write this in the equivalent form $\frac{(\partial E)_p}{(\partial \tau)_p}$,

Ψ $[\partial/\partial p (\partial v/\partial p)_\tau]_\psi = (\partial^2 v/\partial p^2)_\tau - \{\partial^2 v/\partial \tau \partial p\} \cdot \{p(\partial v/\partial p)_\tau\} / \{s + p(\partial v/\partial \tau)_p\}$
constant:

$$[\partial/\partial p (\partial v/\partial \tau)_p]_\psi = \partial^2 v/\partial p \partial \tau - \{(\partial^2 v/\partial \tau^2)_p\} \times$$

$$\{p(\partial v/\partial p)_\tau\} / \{s + p(\partial v/\partial \tau)_p\},$$

$$(\partial C_p/\partial p)_\psi = -\tau(\partial^2 v/\partial \tau^2)_p - \{(\partial C_p/\partial \tau)_p\} \times$$

$$\{p(\partial v/\partial p)_\tau\} / \{s + p(\partial v/\partial \tau)_p\}.$$

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